



EUROPEAN PATENT SPECIFICATION

Date of publication of patent specification: **19.04.95** Int. Cl.⁶: **C08F 2/34, C08F 10/00**

Application number: **91302774.4**

Date of filing: **28.03.91**

Gas phase olefin polymerization process.

Priority: **11.04.90 FR 9004916**

Date of publication of application:
23.10.91 Bulletin 91/43

Publication of the grant of the patent:
19.04.95 Bulletin 95/16

Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

References cited:
EP-A- 0 229 368
EP-A- 0 232 701

Proprietor: **BP Chemicals Limited**
Belgrave House
76 Buckingham Palace Road
London, SW1W 0SU (GB)

Designated Contracting States:
BE CH DE DK ES GB GR IT LI LU NL SE AT

Proprietor: **BP CHEMICALS S.N.C.**
Tour Neptune
la Défense 1,
20, Place de Seine
F-92400 Courbevoie (FR)

Designated Contracting States:
FR

Inventor: **Daire, Erick, BP Chemicals S.N.C.**
Centre de Recherches,
Service Propriete Ind.
BP No. 6,
F-13117 Lavera (FR)
Inventor: **Speakman, John Gabriel, BP Chemi-**
cals S.N.C.
Centre de Recherches,
Service Propriete Ind.
BP No. 6,
F-13117 Lavera (FR)

Representative: **Denbigh, Keith Warwick et al**
BP INTERNATIONAL LIMITED
Patents & Agreements Division
Chertsey Road
Sunbury-on-Thames
Middlesex, TW16 7LN (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

The invention relates to a process for the gas phase polymerization of alpha-olefins which involves a prepolymerization step and the use of an alpha-olefin prepolymer. The process of the invention is particularly applicable to the gas phase polymerization of ethylene, propylene or 1-butene, or mixed with each other and/or optionally with other alpha-olefins such as 1-hexene, 1-octene or 4-methyl-1-pentene.

It is known to polymerize one or more alpha-olefins from a reaction gas mixture containing the alpha-olefin(s) to be polymerized, in a fluidized bed reactor where the polymer particles being formed are maintained in the fluidized state by means of the reaction gas mixture travelling in an upward stream. The gas mixture leaving at the top of the fluidized bed reactor is recycled to the bottom of the latter by means of a gas recycling conduit and of a compressor. During this recycling the gas mixture is most frequently cooled with the aid of a heat exchanger so as to remove the heat produced during the polymerization reaction and to keep constant the polymerization temperature in the fluidized bed.

It is known to carry out the polymerization reaction by using a prepolymer powder prepared beforehand during a prepolymerization stage, with the aid of a catalyst system of Ziegler-Natta type consisting of a solid catalyst based on a transition metal and of a cocatalyst comprising an organometallic compound. The prepolymer powder may also be prepared with the aid of a high-activity catalyst comprising a chromium oxide supported on a granular carrier based on a refractory oxide and activated by a heat treatment. However, when such a process is carried out, it is possible to observe that polymer particles can adhere to the reactor wall and form sheets of polymer. This phenomenon is particularly inopportune because of the fact that these sheets can suddenly become detached from the reactor wall, fall into the bed and thus cause the stoppage of the polymerization reactor. Furthermore, the prepolymer powder can exhibit relatively mediocre dry flow properties and can make it difficult to introduce it into the gas phase polymerization reactor. The disturbing consequences resulting from an irregular feed of catalyst or of prepolymer to a gas phase polymerization reactor are generally known, and especially the risks of formation of hot spots and of agglomerates of molten polymer in the fluidized bed.

European Patent Application EP-A-0,232,701 also discloses a process which makes it possible to manufacture ethylene polymers in a gas phase polymerization reactor with the aid of a catalyst of Ziegler-Natta type, a cocatalyst and an antistatic agent, which are introduced into the reactor separately from each other requiring simultaneous control of the feeds of these three constituents. Furthermore, the antistatic agent introduced into the reactor in the form of a solution in a paraffin-based oil is difficult to disperse in the bed and its efficiency is weakened thereby. In addition, the process may also comprise a stage of treatment of the reactor using the antistatic agent, before the introduction of the catalyst into the reactor and before the startup of the reaction. This preliminary stage correspondingly shortens the time devoted to the production of polyethylene.

An alpha-olefin (co-)polymerization process has now been found, which is carried out in a gas phase polymerization reactor and which makes it possible in particular to avoid the formation of polymer sheets without encountering the disadvantages referred to above. In particular, this process makes use of a catalyst, an organometallic compound and an antistatic agent which are introduced together into the polymerization reactor by means of a single feed. Furthermore, it employs prepolymers which have excellent dry flow properties.

The subject of the invention is therefore a process for gas phase (co-)polymerization of one or more alpha-olefins with the aid of a prepolymer containing a catalyst based on a transition metal belonging to one of the groups IV, V or VI of the Periodic Classification of the elements and an organometallic compound of a metal of group II or III of the said Periodic Classification, the prepolymer being obtained in the course of a prepolymerization carried out before the (co-)polymerization by bringing the said catalyst into contact with one or more alpha-olefins and with the said organometallic compound, which process is characterized in that the prepolymer introduced into the gas phase (co-)polymerization comprises an antistatic agent.

According to the invention it is essential that the gas phase (co-)polymerization of alpha-olefins should be carried out with the aid of a prepolymer containing simultaneously at least one antistatic agent and at least one organometallic compound. It has been found that such a prepolymer is not only highly active in the gas phase (co-)polymerization of alpha-olefins, but that it also permits the manufacture of polyolefin powders having a reduced amount of sheets and agglomerates. Thus, the present invention is based on the astonishing discovery that the catalytic activity of the prepolymer is not substantially decreased and can even be appreciably increased when the prepolymer contains an antistatic agent and an organometallic compound. Particularly, a catalytic activity increasing can be observed, when the antistatic agent comprises at least one metal salt of an organic carboxylic acid, such as a fatty carboxylic acid, e.g. of 8-30 carbon atoms, the salt having usually a molecular weight from 150 to 1200 and the metal being usually an alkali

metal, alkaline earth metal, Cu, Zn, Cd, Al, Pb, Cr, Mo or Mn, or a metal salt, e.g. a Cr salt of a C₁₀ - C₂₀ alkyl- or alkenyl-substituted aromatic carboxylic acid, or a Cr salt of an N-alkyl or N-alkenyl-salicylic acid, or a Cr salt of stearyl-anthranilic acid, or an alkali or alkaline earth metal salt, e.g. Na, K or Ca, of an alkylcarboxylate-substituted sulphonic acid, e.g. a Ca dialkylsulphosuccinate. The antistatic agent may
 5 interact physically with the prepolymer, or chemically or physically with the organometallic compound or catalyst.

According to the invention the antistatic agent present in the prepolymer is a composition, a product or a compound which is capable of limiting the phenomena linked with static electricity. In particular, the antistatic agent makes it possible to avoid the agglomeration of polyolefin particles with each other and to
 10 reduce the formation of polymer sheeting on the walls of the polymerization reactor. The antistatic agent can be one of the antistatic agents known to be used with polyolefins, e.g. polyethylene or polypropylene, in particular those mentioned in the periodical *Kunststoffe* 67 (1977), 3, pages 154 to 159, or in British Patent GB-A-1,402,802, the disclosures of which are hereby incorporated by reference. The antistatic agent can preferably be a composition or a mixture containing at least one metal salt of an organic carboxylic acid,
 15 such as a fatty carboxylic acid, e.g. of 8-30 carbon atoms, the salt usually having a molecular weight from 150 to 1200, e.g. 200 to 800 and the metal being usually an alkali metal, an alkaline earth metal, Cu, Zn, Cd, Al, Pb, Cr, Mo or Mn, preferably Na, K, Ca or Cr; particularly, the metal salt may be an alkali or alkaline earth salt, e.g. Na, K or Ca, of a C₁₂ - C₂₂ fatty carboxylic acid. The metal salt also may be a metal salt, e.g. a Cr salt, of a C₁₀ - C₂₀ alkyl- or alkenyl-substituted aromatic carboxylic acid, preferably with a
 20 hydroxyl or amino substituent, or a metal salt, e.g. a Cr salt of an N-alkyl- or N-alkenyl-anthranilic acid, e.g. a Cr salt of a C₁₄ - C₁₈ alkyl-salicylic acid, or a Cr salt of stearyl-anthranilic acid. The metal salt may also be an alkali or alkaline earth metal salt, e.g. an Na, K or Ca salt, of an alkylcarboxylate-substituted sulphonic acid, preferably a di-(C₂ - C₁₂ alkylcarboxylate)-substituted aliphatic sulphonic acid, especially a di-(C₂ - C₁₂ alkyl) sulphosuccinate, e.g. an Na, K or Ca dihexyl-, or dioctyl-, or didecyl-, or di-2-ethylhexyl
 25 sulphosuccinate.

The antistatic agent may also comprise an alkylated phytic acid polyethylene imine salt or a quaternary ammonium salt of phytic acid. Also, it may comprise a polyelectrolyte such as a copolymer of (i) an ethylenically unsaturated carboxylic acid, e.g. of 2-6 carbon atoms, or an ethylenically unsaturated ester, e.g. with 3-22 carbon atoms, with (ii) an ethylenically unsaturated organic base, e.g. of 6-10 carbon atoms,
 30 e.g. a copolymer of (i) a C₁₀ - C₂₄ alkyl methacrylate with (ii) 2-methyl-5-vinylpyridine. The antistatic agent may also comprise a salt of a sulphonic acid ester, a polyethylene glycol ester of a fatty carboxylic acid, e.g. of 12-22 carbon atoms, or a polyoxyethylene alkyl ether.

Commercial antistatic agents can advantageously be employed, such as "ASA3" (R) sold by SHELL (Holland) which is believed to be a mixture of a Cr salt of C₁₄ - C₁₈ alkyl-salicylic acid, a Ca
 35 dialkylsulphosuccinate and a copolymer of alkylmethacrylate with 2-methyl-5-vinylpyridine in solution in xylene, or "KEROSTAT CE 4009" (R) or "KEROSTAT CE 5009" (R) described in European Patent Applications EP-A-0232701 and EP-A-0229368 and sold by BASF (Germany) which are believed to be a mixture of Cr N-oleylanthranilate, Ca salt of a Medialan acid and di-tert. butylphenol.

The quantity of antistatic agent which is present in the prepolymer can depend on the nature of the
 40 antistatic agent and on that of the prepolymer, and on the type of catalyst. An antistatically effective amount is generally such that the prepolymer contains from 0.01 to 10 mg, preferably from 0.02 to 5 mg and more particularly from 0.025 to 1 mg of an antistatic agent per gram of prepolymer. It is known that a quantity which is too small has no effect against the formation of polymer sheets, while a quantity which is too great results in prepolymers of an adhesive nature which are difficult to employ in a gas phase polymerization
 45 reaction, especially in a fluidized bed.

The prepolymer additionally contains an organometallic compound of a metal of group II or III of the Periodic Classification of the elements. It is generally chosen from organoaluminium, organomagnesium or organozinc compounds. The organometallic compound may be a trialkylaluminium of general formula:



in which R denotes an alkyl radical containing from 1 to 12, e.g. 2 to 8 carbon atoms, such as triethylaluminium, triisobutylaluminium, tri-n-hexylaluminium or tri-n-octylaluminium. It may also be an alkylaluminium halide or alcoholate of general formula:

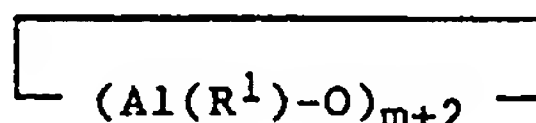


in which X is a chlorine or bromine atom or an alkoxy radical containing 1 to 8, e.g. 1 to 4 carbon atoms, R

is an alkyl radical containing from 1 to 12, e.g. 2 to 8 carbon atoms and n is a whole or fractional number equal to or greater than 0.05 and smaller than 3, e.g. 0.05 to 2, particularly 0.1 to 1. It may be chosen from diethylaluminium monochloride, ethylaluminium sesquichloride, diisobutylaluminium monochloride and ethoxydiethylaluminium. It may also be an alkylenealuminium, e.g. an isoprenylaluminium, or an aluminoxane. The latter may be either a linear aluminoxane corresponding to the general formula:



in which R^1 denotes an alkyl radical, e.g. of 1 to 6 carbon atoms, such as methyl or ethyl, and m is a number ranging from 2 to 40, preferably from 10 to 20, or a cyclic aluminoxane corresponding to the general formula:



in which R^1 and m are as defined above. Preferably, the aluminoxane is a methylaluminoxane.

The prepolymer used in the process of the invention is prepared during a prepolymerization stage which may be carried out by batchwise or continuously. The prepolymerization consists in bringing the catalyst into contact with at least one organometallic compound and at least one alpha-olefin containing from 2 to 12 carbon atoms, in particular with ethylene, propylene or 1-butene, or mixed with each other and/or with other C_5-C_{12} alpha-olefins such as 1-hexene, 4-methyl-1-pentene, 1-octene or 1-dodecene. The quantity of the organometallic compound(s) used in the prepolymerization is such that the atomic ratio of the quantity of the metal(s) of the said organometallic compound(s) to the quantity of the transition metal(s) of the catalyst is of 0.01 to 100, preferably 0.1 to 50, more particularly 0.2 to 10, e.g. 0.5 to 5. The prepolymerization may be carried out in various ways. In particular, it may be carried out in a slurry in a hydrocarbon liquid such as a liquid alpha-olefin, or an inert saturated hydrocarbon liquid such as n-pentane, isopentane, n-hexane or n-heptane. It may also be carried out in the gaseous phase in a fluidized-bed reactor and/or one fitted with a mechanical stirrer. The prepolymerization temperature is lower than that at which the prepolymer particles begin to soften. It is generally from 0 to 115°C, preferably from 25 to 100°C, e.g. 40 to 80°C. The prepolymerization may be carried out in one or more stages. It is usually stopped when the prepolymer contains from 0.1 to 500 g, preferably from 1 to 300g, e.g. 10 to 250g of polymer per milligram atom of transition metal. In addition, the prepolymerization may be carried out in the presence of a chain-limiting agent, such as hydrogen, in order to control the molecular weight of the prepolymer.

According to the process of the invention the antistatic agent may be brought into contact with the catalyst and the organometallic compound(s) before and/or during the prepolymerization, preferably in the beginning of the prepolymerization, and/or with the prepolymer after the prepolymerization but before the introduction of the prepolymer into the gas phase polymerization medium. The total quantity of antistatic agent to be used is from 0.1 to 200 g, preferably from 0.2 to 100g, e.g. 0.5 to 50g per gram atom of transition metal present in the catalyst or the prepolymer. The antistatic agent may be present in the prepolymer in a quantity of 0.05 to 200g, preferably 0.1 to 100g, particularly 0.2 to 50g per gram atom of the metal(s) of the organometallic compound(s) present in the prepolymer or during the prepolymerization.

More particularly, the antistatic agent may be brought into contact with (a) a catalyst based on at least one transition metal belonging to one of the Groups IV, V or VI of the Periodic Classification of the elements and (b) at least one organometallic compound of a metal of Group II or III of the said Periodic Classification, before and/or during a prepolymerization comprising bringing the said catalyst into contact with at least one C_2-C_{12} alpha-olefin and with the said organometallic compound, in quantities of from 0.1 to 200g of the antistatic agent per gram atom of the transition metal of the said catalyst and from 0.01 to 100 moles of the said organometallic compound per gram atom of the transition metal of the said catalyst, the prepolymerization being carried out until from 0.1 to 500g of prepolymer are obtained per milligram atom of the transition metal of the said catalyst.

In practice, the contact between the antistatic agent, the catalyst and the organometallic compound can be brought about in various possible ways. It is preferred to produce the contact in the presence of a hydrocarbon liquid, in which the antistatic agent can be in solution or in which the prepolymerization is carried out in suspension. The hydrocarbon liquid may be a liquid alpha-olefin, e.g. of 2 to 12, preferably 3 to 12 carbon atoms or preferably one or more inert saturated hydrocarbons, such as cycloalkanes or alkanes such as n-pentane, isopentane, n-hexane or n-heptane. In this way, it has been found that the

antistatic agent is dispersed uniformly not only at the surface of the prepolymer particles but also inside them, surprisingly, without usually appreciably diminishing the efficiency of the antistatic agent during the gas phase (co-)polymerization.

The contact of the antistatic agent with the prepolymer after the prepolymerization can also be brought about according to various methods. The antistatic agent may be brought into contact with a prepolymer obtained after a prepolymerization comprising bringing into contact a catalyst based on at least one transition metal belonging to one of the Groups IV, V or VI of the Periodic Classification of the elements with at least one organometallic compound of a metal of Group II or III of the said Periodic Classification and with at least one C_2-C_{12} alpha-olefin, the prepolymer comprising from 0.002 to 10 milligram atoms of the transition metal of the said catalyst and having an atomic ratio of the metal of the said organometallic compound to the transition metal of the said catalyst from 0.01 to 100, the antistatic agent being contacted with the prepolymer in an amount from 0.1 to 200g per gram atom of the transition metal contained in the prepolymer. The contact of the antistatic agent with the prepolymer can be produced in particular by dry blending of the antistatic agent with the prepolymer. However, it is preferred to bring the antistatic agent into contact with the prepolymer in the presence of a hydrocarbon liquid which may be identical to that employed during the prepolymerization, e.g. a liquid alpha-olefin or an inert liquid saturated hydrocarbon. This presents the advantage of dispersing the antistatic agent in all the prepolymer particles, and in particular the finest particles which are generally the major source of the static electricity and can promote the formation of polymer agglomerates.

The antistatic agent contacting may be preferably carried out by a combination of the two preceding methods, i.e. by contacting the antistatic agent (i) first of all with the catalyst and the organometallic compound before or during a prepolymerization, and then (ii) with the prepolymer after the prepolymerization. More particularly, the antistatic agent may be (i) first of all brought into contact with (a) a catalyst based on at least one transition metal belonging to one of the Groups IV, V or VI of the Periodic Classification of the elements and (b) at least one organometallic compound of a metal of Group II or III of the said Periodic Classification before or during a prepolymerization, preferably at the beginning of a prepolymerization comprising bringing the said catalyst into contact with at least one C_2-C_{12} alpha-olefin and with the said organometallic compound, in quantities of from 0.05 to 100g, preferably from 0.1 to 50g, e.g. 0.5 to 20g of the antistatic agent per gram atom of the transition metal of the said catalyst and from 0.01 to 100 moles of the said organometallic compound per gram atom of the transition metal of the said catalyst, the prepolymerization being carried out until from 0.1 to 500g of prepolymer are obtained per milligram atom of the transition metal of the said catalyst, and (ii) then brought into contact with the prepolymer obtained after the end of the prepolymerization in a quantity ranging from 0.05 to 100g, preferably from 0.1 to 50g, e.g. 5 to 50g of the antistatic agent per gram atom of the transition metal contained in the prepolymer. The contacting of the antistatic agent with (a) the catalyst and (b) the organometallic compound before or during the prepolymerization and the contacting of the antistatic agent with the prepolymer after the end of the prepolymerization may be carried out in the presence of a liquid hydrocarbon which is either an inert saturated hydrocarbon or an alpha-olefin. This particular process presents the advantage of dispersing the antistatic agent easily in the prepolymer and of obtaining a prepolymer containing an antistatic agent which is dispersed uniformly both inside and at the surface of the prepolymer particles.

The prepolymer thus obtained according to the invention is catalytically active in an alpha-olefin (co-)polymerization. It consists of particles with a mass-mean diameter ranging from 50 to 500 microns, preferably from 100 to 300 microns. It comprises per gram of prepolymer from 0.002 to 10, preferably from 0.003 to 0.1 milligram atoms of at least one transition metal belonging to one of groups IV, V or VI of the Periodic Classification of the elements, such as titanium, vanadium, hafnium, zirconium or chromium. It also comprises, per gram of prepolymer, at least one organometallic compound of a metal of Group II or III of the said Periodic Classification, such as aluminium, magnesium or zinc, in an atomic ratio of the metal(s) of the organometallic compound(s) to the transition metal(s) of 0.01 to 100, preferably of 0.1 to 50, e.g. 0.2 to 10 or 0.5 to 5. In addition, the antistatic agent is present in the prepolymer in an amount as specified above. The prepolymer may be used in the gas phase (co-)polymerization in the form of a dry powder which has a bulk density at rest of 0.3 to 0.55 g/cm³, preferably of 0.35 to 0.52 g/cm³. The prepolymer powder has excellent dry flow properties, as given by the flowability test described later, the prepolymer powder passing particularly freely under gravity through the lower orifice of a hopper whose diameter is smaller than or equal to 20 mm, preferably from 5 to 15mm, the hopper having the shape of a conical frustum with a vertical axis and an apex angle of 30° pointing downwards.

The catalyst used during the prepolymerization stage can be a catalyst comprising a chromium oxide supported on a refractory oxide, e.g. silica, alumina, or silico-alumina, and activated by a heat treatment

under a nonreductive atmosphere. This catalyst may be in particular one of those described in French Patent Applications FR-A-2,609,036 and FR-A-2,570,381.

The catalyst may also be a catalyst of Ziegler-Natta type based on at least one transition metal, preferably selected amongst titanium, vanadium, hafnium, chromium or zirconium. It may be a metallocene catalyst based on chromium or zirconium, i.e. a chromocene or zirconocene catalyst. The catalyst may contain halogen atoms, e.g. chlorine or bromine atoms. The catalyst may contain or be supported on a magnesium compound, e.g. a magnesium oxide, a magnesium hydroxide, a magnesium alkoxide, or a magnesium chloride. It may contain or be supported on a refractory oxide, e.g. silica, alumina, or silico-alumina. The catalyst may in particular correspond to the general formula



in which Me is an aluminium and/or zinc atom, M is an atom of a transition metal belonging to the groups IV, V or VI of the Periodic Classification of the elements, preferably a titanium and/or vanadium atom, R_1 is an alkyl group containing from 1 or 2 to 14, e.g. 2 to 6 carbon atoms, R_2 is an alkyl group containing from 1 or 2 to 12, e.g. 2 to 6 carbon atoms, X is a chlorine and/or bromine atom, D is an electron-donor compound comprising at least one oxygen or sulphur or nitrogen or phosphorus atom, preferably free from labile hydrogen, with

m from 0.5 to 50, preferably from 1 to 10,
n from 0 to 1, preferably from 0 to 0.5,
p from 0 to 3, preferably from 0 to 2,
q from 0 to 1, preferably from 0 to 0.5,
r from 2 to 104, preferably from 3 to 24, and
s from 0 to 60, preferably from 0 to 20.

The catalyst may be obtained by various processes, especially by those according to which a magnesium compound such as magnesium chloride is milled in the presence of at least one transition metal compound, or else a magnesium compound is precipitated at the same time as one or more transition metal compounds. It may also be prepared by precipitation of a transition metal compound onto solid particles consisting essentially of magnesium chloride, which can be obtained by reaction of an organomagnesium compound with an organic chlorine compound. The precipitation of the transition metal compound onto the solid particles of magnesium chloride may be carried out by reaction of reduction of a transition metal compound taken at the maximum valency with the aid of organometallic compounds of metals of groups II and III of the Periodic Classification of the elements. This reduction reaction can be carried out at a temperature of between -30°C and $+100^\circ\text{C}$ with agitating, e.g. stirring in a liquid hydrocarbon medium and optionally in the presence of an electron-donor compound D, preferably free from labile hydrogen, which may be chosen from a wide variety of products, such as amines, amides, phosphines, sulphoxides, sulphones, esters, thioethers, ethers, e.g. aliphatic ethers, cyclic or non-cyclic ethers.

The catalyst may in particular be prepared according to one of the processes described in French Patent Applications FR-A-2,099,311, FR-A-2,116,698 and FR-A-2,628,110.

The catalyst of Ziegler-Natta type may also include a support based on a refractory oxide such as a silica, an alumina or a mixture of these two oxides. In particular, it may be prepared according to a process which consists:

a) in a first stage, in bringing a granular support based on refractory oxide comprising hydroxyl groups into contact with a dialkylmagnesium and optionally a trialkylaluminium,
b) in a second stage, in bringing the product resulting from the first stage into contact with a monochloro organic compound selected amongst primary, preferably secondary or tertiary alkyl or cycloalkyl monochlorides containing 2 to 19, preferably 3 to 19 carbon atoms and amongst compounds of general formulae



in which R_6 is an aryl radical containing from 6 to 16, e.g. 6 to 10 carbon atoms, R_7 and R_8 being identical or different radicals chosen from hydrogen, alkyl radicals containing from 1 to 6, e.g. 1 to 4 carbon atoms and aryl radicals containing from 6 to 16, e.g. 6 to 10 carbon atoms, identical to or different from R_6 , and

(c) in a third stage, in bringing the product resulting from the second stage into contact with at least one tetravalent titanium or vanadium compound or a trivalent vanadyl compound, e.g. TiCl_4 , VCl_4 or VOCl_3 .

When the catalyst contains magnesium, chlorine, titanium and/or vanadium, and especially a support based on a refractory oxide, e.g. silica, alumina, or silico-alumina, and when, according to the invention, it is converted into a prepolymer containing an antistatic agent, unexpectedly it can exhibit a catalytic activity in gas phase (co-)polymerization of ethylene which is considerably increased. In particular, the activity of the prepolymer may be from 2 to 3 times greater than that of a prepolymer prepared in the same conditions but without antistatic agent. When a catalyst, whether of Ziegler-Natta type or chromium oxide type, is supported on a refractory oxide, one gram of prepolymer may comprise from 2 to 10,000 mg, preferably 3 to 1,000 mg, particularly 4 to 200 mg of a refractory oxide, such as silica, alumina or silico-alumina.

The prepolymer according to the present invention can be introduced into the gas phase polymerization medium either in the form of a slurry in a hydrocarbon liquid such as an inert saturated hydrocarbon or an alpha-olefin, or in the form of a dry powder. When the prepolymerization is carried out in a slurry in a hydrocarbon liquid, the prepolymer slurry can be used as such and directly introduced into the gas phase polymerization medium. The prepolymer can be also separated from the hydrocarbon liquid, preferably by evaporating off the said hydrocarbon liquid under an inert atmosphere, e.g. nitrogen, more particularly under a partial vacuum. Thus, the prepolymer is obtained in the form of a dry powder which can be used as such and directly introduced into the gas phase polymerization medium. When the prepolymerization is carried out in a gas phase, the prepolymer is obtained in the form of a dry powder which can be used as such and directly introduced into the gas phase polymerization medium. The antistatic agent which can be added to and blended with the prepolymer after the prepolymerization, but prior to the gas phase (co-)polymerization, can be contacted with the prepolymer dry powder or preferably with the prepolymer slurry. After the contacting of the antistatic agent with the prepolymer slurry, the prepolymer can be separated from the hydrocarbon liquid of the slurry, preferably by evaporating off the said hydrocarbon liquid under an inert atmosphere, and thus the prepolymer can be obtained in the form of a dry powder.

The gas phase (co-)polymerization may be carried out in a reactor fitted with a mechanical stirrer for dry powder, or, preferably, in a fluidized bed reactor in which the (co)polymer particles being formed are maintained in the fluidized state with the aid of an upward gas stream propelled at a velocity of 2 to 10 times, preferably 5 to 8 times the minimum fluidization velocity. The velocity may be between 15 and 100 cm/s, preferably between 40 and 70 cm/s. The upward gas stream consists of a reaction gas mixture which comprises in particular the alpha-olefin(s) to be (co-)polymerized and optionally a diene, a chain-limiting agent such as hydrogen and an inert gas such as nitrogen, ethane or other higher alkanes. On passing through the fluidized bed, only part of the alpha-olefin(s) is (co-)polymerized in contact with the growing (co-)polymer particles. The fraction of alpha-olefins which has not reacted leaves the fluidized bed and passes through a cooling system intended to remove the heat produced during the reaction, before being recycled to the fluidized bed reactor by means of a compressor.

The average pressure in the reactor may be close to atmospheric pressure but is preferably higher, in order to increase the polymerization rate. It may be between 0.1 and 5 MPa, preferably between 0.2 and 3 MPa.

The temperature is maintained in the reactor at a sufficient level for the (co-)polymerization to be fast without, however, being too close to the softening temperature of the polymer. It is generally of 0 to 135 °C, preferably 20 to 110 °C, e.g. 70 to 110 °C.

In practice the prepolymer may be introduced into the reactor in the form of a dry powder or as a slurry in an inert liquid saturated hydrocarbon or in a liquid alpha-olefin. The introduction of the prepolymer may be carried out continuously or intermittently. The withdrawal of the (co-)polymer manufactured may also be carried out continuously or intermittently.

An additional organometallic compound of a metal belonging to group II or III of the Periodic Classification of the elements, in particular an organoaluminium, an organomagnesium or an organozinc compound may be introduced into the reactor during the gas phase (co-)polymerization. It may be identical to or different from that contained in the prepolymer. The additional organometallic compound may be introduced into the polymerization reactor in the liquid state or in the gaseous state, and may also be added to the prepolymer before it is introduced into the gas phase polymerization reactor. An electron-donor compound, e.g. of the above mentioned formula D, may also be used. The latter may be added to the prepolymer before it is introduced into the gas phase polymerization reactor. It may also be directly introduced into the polymerization reactor or mixed with the additional organometallic compound.

According to the process of the present invention it is possible to polymerize or copolymerize alpha-olefins containing from 2 to 12 carbon atoms, in particular ethylene, propylene or 1-butene, or mixed with each other and/or with other C₅ - C₁₂ alpha-olefins such as 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene or 1-dodecene, or with dienes. The process is very particularly suitable for the gas phase polymerization or copolymerization of ethylene or propylene in a fluidized bed.

Determination of the flowability of a prepolymer powder

The flowability of a prepolymer powder is determined with the aid of a series of eight hoppers which are in the shape of a conical frustum of revolution, with a vertical axis and with an apex angle of 30° pointing downwards. These hoppers differ from each other in the diameter of the small circular base, corresponding to the lower orifice of the hopper, this diameter being equal to 5, 10, 15, 20, 25, 30, 35 or 40 mm, and in the height of the conical frustum, equal to 107, 100, 90, 80, 73, 65, 58 or 52 mm respectively.

The lower orifice of the hopper is closed by means of a glass plate. The prepolymer powder which has been aerated and loosened beforehand is poured into the hopper through the upper orifice without being packed. When the hopper is filled, the powder is levelled at the height of the upper orifice of the hopper by trimming off horizontally the excess quantity of poured powder. The glass plate closing the lower orifice is then withdrawn and it is ascertained whether free flow of the powder takes place or not.

The flowability of a prepolymer powder is determined by the smallest value of the diameter of the lower orifice through which the powder is capable of flowing freely under gravity. According to this method a prepolymer powder is considered as having a good flow property when it runs freely under gravity through the lower orifice of the hopper with a diameter smaller than or equal to 20 mm.

The following nonlimiting examples illustrate the present invention.

Example 1

Preparation of an ethylene prepolymer in suspension in n-hexane

Into a stainless steel 1000-litre reactor equipped with a jacket and with a stirrer rotating at 140 revolutions per minute and maintained at 30°C were introduced under nitrogen atmosphere, successively, 500 litres of n-hexane, 1 litre of an n-hexane solution containing 17.5 g of an antistatic agent of trademark "ASA 3" sold by Shell Company (Holland), 0.6 litres of a solution containing 1 mole/litre of tri-n-octylaluminium in n-hexane and, lastly, a quantity of a catalyst prepared exactly as in Example 1 of French Patent Application FR-A-2,570,381 and containing 2.3 gram atoms of chromium. The reactor was then heated to 75°C and ethylene was introduced therein at a substantially constant rate of 15 kg/h for 8 hours. At the end of this time a suspension of prepolymer was obtained, which was maintained at the temperature of 75°C for 30 minutes in order to consume as much unreacted ethylene as possible. The reactor was then degassed and then cooled to 60°C.

To the prepolymer suspension was added 300 litres of n-hexane preheated to 60°C, 0.3 mole of tri-n-octylaluminium and 10 g of "ASA 3". The prepolymer suspension was kept stirred for 15 minutes under these conditions. After settling for 15 minutes, approximately 300 litres of liquid were extracted from this suspension. The whole of this operation was repeated 4 times and the prepolymer suspension was then cooled to room temperature (20°C) and 0.8 mole of tri-n-octylaluminium were added to it. After drying under nitrogen approximately 120 kg of a prepolymer were obtained, consisting of a nonadhesive powder which had very good dry flow properties and a bulk density of 0.4 g/cm³. This powder consisted of particles which had a mass-mean diameter of 250 microns and contained 0.019 milligram atoms of chromium, 0.021 milligram atoms of aluminium and 0.48 mg of antistatic agent per gram of prepolymer.

Polymerization of ethylene in a fluidized bed

The operation was carried out with the aid of a stainless steel fluidized reactor of 45 cm diameter, the fluidization being produced by a rising gas mixture propelled at a velocity of 52 cm/s and at a temperature of 108°C. The gas mixture consisted of hydrogen, ethylene and nitrogen, the partial pressures (pp) of these three constituents being the following:

50

hydrogen pp :	0.36 MPa
ethylene pp :	1.05 MPa
nitrogen pp :	0.593 MPa

70 kg of a degassed and anhydrous polyethylene powder were introduced into this reactor as a powder charge, followed by 1 litre of a molar solution of tri-n-octylaluminium in n-hexane. 4 g of the prepolymer prepared previously were then introduced into this reactor sequentially at a frequency of once every 5 minutes.

EP 0 453 116 B1

At the end of approximately 3 hours, the polyethylene output having become steady, 10 ml/h of a molar solution of tri-n-octylaluminium in n-hexane were introduced continuously into the reactor. In these conditions, approximately 28 kg/h of a polyethylene powder were collected by sequential withdrawal, and no formation of polyethylene sheets along the reactor wall was observed. After 8 hours' operation, the powder charge introduced initially into the reactor was practically completely removed and a polyethylene powder was obtained which had the following characteristics:

- density:	0.953g/cm ³ (at 20 ° C)
- chromium content:	lower than 2 ppm
- melt index (MI5) measured at 190 ° C under a 5 kg load according to ASTM-D-1238 condition P:	1.5g/10 minutes
- bulk density:	0.40 g/cm ³
- molecular weight distribution (Mw/Mn):	7.7.

Example 2

Preparation of an ethylene prepolymer in suspension in n-hexane

The operation was carried out exactly as in Example 1.

Copolymerization of ethylene with 1-butene in a fluidized bed

The operation was carried out with the aid of a stainless steel fluidized bed reactor of 45 cm diameter, the fluidization being produced by a rising gas mixture propelled at a velocity of 52 cm/s at a temperature of 90 ° C; the gas mixture consisted of hydrogen, ethylene, 1-butene and nitrogen, the partial pressures (pp) of these four constituents being the following:

hydrogen pp:	0.204 MPa
ethylene pp:	1.05 MPa
1-butene pp:	0.021 MPa
nitrogen pp:	0.725 MPa

70 kg of a degassed and anhydrous polyethylene powder were introduced into the reactor as a powder charge, followed by 1 litre of a molar solution of tri-n-octylaluminium in n-hexane. 3.2 g of the prepolymer prepared previously were then introduced into this reactor sequentially at a frequency of once every 5 minutes.

At the end of approximately 3 hours the output of copolymer of ethylene and 1-butene having become steady, 10 ml/h of a molar solution of tri-n-octylaluminium in n-hexane were introduced continuously into the reactor. Approximately 30 kg/h of a copolymer powder were collected under these conditions by sequential withdrawal, and no formation of copolymer sheets along the reactor wall was observed. After 8 hours' operation under these conditions the powder charge introduced initially into the reactor was practically completely removed and a powder of copolymer of ethylene and 1-butene which had the following characteristics was obtained:

- density:	0.938g/cm ³ (at 20 ° C)
- weight content of 1-butene-derived unit:	1.3%
- chromium content:	less than 2 ppm.

Example 3Preparation of a catalyst

5 A granular support is employed, consisting of a silica powder sold under the trademark "SG 332" by W.R. Grace Company (USA) which had a specific surface area (BET) of 300 m²/g and a pore volume of 1.7 ml/g. It consisted of particles which had a mass-mean diameter of 80 microns. It was dried for 5 hours at 200 °C under an air atmosphere and a silica powder rid of free water and containing approximately 2 millimoles of hydroxyl group per gram was obtained. All the subsequent operations were carried out under
10 a nitrogen atmosphere.

600 ml of n-hexane and 60 g of the silica dried previously were introduced into a stainless steel 1-litre reactor fitted with a stirrer rotating at 250 revolutions per minute, followed slowly over 1 hour by 138.6 millimoles of dibutylmagnesium, at a temperature of 20 °C. The mixture thus obtained was stirred for 1 hour at 20 °C and a solid product (A) was obtained.

15 The reactor containing the suspension of the solid product (A) in n-hexane was then heated to 50 °C. 277.2 millimoles of tert-butyl chloride were introduced slowly into the reactor over 1 hour with stirring. At end of this time the mixture was stirred for one hour at 50 °C, then cooled to room temperature (20 °C). A suspension of a solid product (B) in n-hexane was obtained, which contained chlorine and magnesium in an atomic ratio Cl/Mg equal to 1.69 and which contained substantially no functional group reductive towards
20 titanium tetrachloride.

The reactor containing the suspension of the solid product (B) in n-hexane was then heated to 50 °C. 69.3 millimoles of titanium tetrachloride were introduced into it slowly over 2 hours. The mixture thus obtained was kept stirred for 1 hour at 50 °C and was then cooled to room temperature. A solid catalyst (C) in suspension in n-hexane was obtained, after three washings each time with 600 ml of n-hexane, contained
25 2.81 milligram atoms of magnesium, 5.7 milligram atoms of chlorine and 0.65 milligram atoms of tetravalent titanium per gram of silica.

Preparation of an ethylene prepolymer in suspension in n-hexane

30 Into a stainless steel 1000-litre reactor equipped with a jacket and a stirrer rotating at 140 revolutions per minute and heated to 70 °C were introduced in succession 450 l of n-hexane, 1 litre of a solution containing 2.8 g of an antistatic agent of trademark "ASA 3" (R) in n-hexane, 3.6 moles of tri-n-octylaluminium and, lastly, a quantity of the catalyst prepared previously, containing 3 gram atoms of titanium. Into this reactor were then introduced a quantity of hydrogen until partial pressure of hydrogen of
35 0.06 MPa was obtained, and ethylene at a substantially constant rate of 15 kg/h for 8 hours. At the end of the second and the fourth hours of reaction, a quantity of hydrogen corresponding to a partial pressure of 0.04 MPa was introduced into the reactor. After 8 hours' reaction the introduction of ethylene was stopped and 67 g of "ASA 3" (R) were introduced into the reactor. A suspension of 120 kg of a prepolymer was obtained, which was kept stirring for 15 minutes. After evaporation of the n-hexane and drying under
40 nitrogen approximately, 120 kg of a nonadhesive prepolymer powder was obtained, which had very good dry flow properties and a bulk density of 0.45g/cm³. This powder consisted of particles which had a mass-mean diameter of 240 microns and contained 0.58 mg of antistatic agent, 0.03 milligram atoms of aluminium and 0.025 milligram atoms of titanium per gram of prepolymer.

45 Polymerization of ethylene in a fluidized bed

The operation was carried out with the aid of a stainless steel fluidized bed reactor of 45 cm diameter, the fluidization being produced by a rising gas stream propelled at a velocity of 40 cm/s at a temperature 85 °C. This gas mixture consisted of hydrogen, ethylene and nitrogen, the partial pressures (pp) of these
50 three constituents being the following:

hydrogen pp:	0.45 MPa
ethylene pp:	0.70 MPa
nitrogen pp:	0.45 MPa

55

100 kg of a degassed and anhydrous polyethylene powder were introduced into the reactor as a powder charge, followed by 0.3 litre of a molar solution of triethylaluminium in n-hexane. Into this reactor

EP 0 453 116 B1

were then introduced, sequentially, at a frequency of once every 5 minutes, 15 g of the prepolymer prepared previously and, continuously, 9 ml/hour of a molar solution of triethylaluminium in n-hexane. The polyethylene produced was recovered by sequential withdrawal in order to keep the fluidized bed at a constant height.

5 After 20 hours' operation under these conditions the powder charge introduced initially into the reactor was practically completely removed and a polyethylene powder which had the following characteristics was recovered at a rate of 18 kg/hour:

10	- density:	0.960g/cm ³ (at 20 ° C)
	- titanium content:	12 parts by weight per million (ppm)
	- silica content:	400 ppm
	- melt index MI2.16 measured at 190 ° C under a 2.16 kg load according to ASTM-D-1238 condition E:	4g/10 minutes.
15	- bulk density:	0.40 g/cm ³
	- molecular weight distribution measured as the Mw/Mn ratio:	5.4.

After 12 days' operation the reaction was stopped and no sheet of polymer was found in the reactor.

20 Example 4

Preparation of a catalyst

25 The operation was carried out exactly as in Example 3.

Preparation of an ethylene prepolymer

The operation was carried out exactly as in Example 3.

30 Copolymerization of ethylene with 1-butene in a fluidized bed

The operation was carried out with the aid of a stainless steel fluidized bed reactor of 45 cm diameter, the fluidization being produced by rising gas mixture propelled at a velocity of 40 cm/s at a temperature of 80 ° C. The gas mixture consisted of hydrogen, ethylene, 1-butene and nitrogen, the partial pressures (pp) of these four constituents being the following:

40	hydrogen pp:	0.42 MPa
	ethylene pp:	0.32 MPa
	1-butene pp:	0.08 MPa
	nitrogen pp:	1.16 MPa

100 kg of a degassed and anhydrous powder of a copolymer of ethylene and 1-butene were introduced into the reactor as a powder charge, followed by 0.3 l of a molar solution of triethylaluminium in n-hexane. Into this reactor were then introduced, sequentially, at a frequency of once every 6 minutes, 15g of the prepolymer prepared previously and, continuously, 9 ml/hour of a molar solution of triethylaluminium in n-hexane. The copolymer produced was recovered by sequential withdrawal to keep the fluidized bed at a constant height.

50 After 15 hours' operation under these conditions the powder charge introduced initially into the reactor was practically completely removed and 20.5 kg/hour of a copolymer of ethylene and 1-butene which had the following characteristics were recovered:

55

- density:	0.919g/cm ³ (at 20 ° C)
- titanium content:	8 ppm
- silica content:	250 ppm
- melt index MI2.16 measured at 190 ° C under a 2.16 load according to ASTM-D-1238 condition E:	1.1 g/10 minutes
- bulk density:	0.30 g/cm ³
- molecular weight distribution measured by the ratio Mw/Mn:	5.4.

After 12 days' operation the reaction was stopped and no sheet of polymer was found in the reactor.

Example 5 (comparative)

Preparation of a catalyst

The operation was carried out exactly as in Example 3.

Preparation of an ethylene prepolymer

The operation was carried out exactly as in Example 3, apart from the fact that no antistatic agent "ASA 3" (R) was employed. The prepolymer thus obtained had a bad flow property, characterised by the fact that it ran freely under gravity through the lower orifice of the hopper with a diameter higher than or equal to 40 mm.

Copolymerization of ethylene with 1-butene in a fluidized bed

The operation was carried out exactly as in Example 4, apart from the fact that the prepolymer prepared above was employed instead of the prepolymer prepared in Example 4.

Under these conditions the copolymer output was 16 kg/h and after 2 days operation a formation of copolymer sheets was observed, which made it necessary to stop the copolymerization reaction.

Example 6

Preparation of an ethylene prepolymer in suspension in n-hexane

Into a stainless steel 1000-litre reactor equipped with a jacket and a stirrer rotating at 140 revolutions per minute and heated to 70 ° C were introduced successively 450 l of n-hexane, 1 litre of a solution containing 3 g of an antistatic agent of trademark "ASA 3" (R) in n-hexane, 3.15 moles of tri-n-octylaluminium and, finally, a quantity of the catalyst prepared exactly as in Example 1(a) of French Patent Application FR-A-2405,961 containing 3 gram atoms of titanium. Into this reactor were introduced a quantity of hydrogen to obtain a partial pressure of hydrogen of 0.01 MPa, and ethylene at a substantially constant rate of 15 kg/h. After 8 hours' reaction the introduction of ethylene was stopped.

A suspension of 120 kg of a prepolymer was obtained, which was kept stirred 15 minutes. After evaporation of the n-hexane and drying under nitrogen, approximately 120 kg of a nonadhesive prepolymer powder was obtained, which had very good dry flow properties and a bulk density of 0.35 g/cm³. This powder consisted of particles which had a mass-mean diameter of 220 microns and contained 0.025 mg of antistatic agent, 0.026 milligram atoms of aluminium and 0.025 milligram atoms of titanium per gram of prepolymer.

Copolymerization of ethylene with 1-butene in a fluidized bed

The operation was carried out with the aid of a stainless steel fluidized bed reactor of 45 cm diameter, the fluidization being produced by a rising gas stream propelled at a velocity of 40 cm/s at a temperature of 80 ° C. This gas mixture consisted of hydrogen, ethylene, 1-butene and nitrogen, the partial pressures (pp) of these four constituents being the following:

EP 0 453 116 B1

hydrogen pp:	0.10 MPa
ethylene pp:	0.56 MPa
1-butene pp:	0.21 MPa
nitrogen pp:	0.73 MPa

5

100 kg of a degassed and anhydrous powder of copolymer of ethylene and 1-butene were introduced into the reactor as a powder charge, followed by 1 litre of a molar solution of triethylaluminium in n-hexane. 15g of the prepolymer prepared beforehand were then introduced into this reactor sequentially at a frequency of once every 5 minutes. The polyethylene produced was recovered by sequential withdrawal to keep the fluidized bed at a constant height.

After 20 hours' operation under these conditions the powder charge introduced initially into the reactor was practically completely removed and a copolymer powder which had the following characteristics was recovered at a rate of 20 kg/hour:

15

- density:	0.918g/cm ³ (at 20 ° C)
- titanium content:	18 ppm
- melt index MI _{2.16} measured at 190 ° C under a 2.16 kg load according to ASTM-D-1238 condition E:	0.9 g/minutes
- bulk density:	0.33 g/cm ³
- molecular weight distribution measured by the ratio Mw/Mn:	4.6

20

After 17 days' operation the reaction was stopped and no copolymer sheet was found in the reactor.

25

Claims

- Prepolymer of one or more C₂-C₁₂ alpha-olefins which is catalytically active in an alpha-olefin (co-)polymerization, the prepolymer consisting of particles with a mass-mean diameter ranging from 50 to 500 microns and comprising from 0.002 to 10 milligram atoms of at least one transition metal belonging to one of Groups IV, V or VI of the Periodic Classification of the elements per gram of prepolymer, an antistatic agent and at least one organometallic compound of a metal of Group II or III of said Periodic Classification in an atomic ratio of the metal(s) of the organometallic compound(s) to the transition metal(s) of 0.01 to 100.
- Prepolymer according to Claim 1, characterised in that it comprises from 0.01 to 10 mg of the antistatic agent per gram of prepolymer.
- Prepolymer according to Claim 1 or 2, characterised in that the antistatic agent comprises at least one of the products or compounds selected amongst:
 - a metal salt of a C₈-C₃₀ carboxylic acid, the metal being an alkali metal, an alkaline earth metal, Cu, Zn, Cd, Al, Pb, Cr, Mo or Mn,
 - a Cr salt of a C₁₀-C₂₀ alkyl- or alkenyl-substituted aromatic carboxylic acid,
 - a Cr salt of an N-alkyl or N-alkenyl-anthranilic acid,
 - an alkali or alkaline earth metal salt of an alkylcarboxylate-substituted sulphonic acid,
 - an alkylated phytic acid polyethylene imine salt,
 - a quaternary ammonium salt of phytic acid,
 - a copolymer of (i) an ethylenically unsaturated carboxylic acid or an ethylenically unsaturated ester with (ii) an ethylenically unsaturated organic base,
 - a salt of a sulphonic acid ester,
 - a polyethylene glycol ester of a fatty carboxylic acid, and
 - a polyoxyethylene alkyl ether.
- Prepolymer according to any of Claims 1 to 3, characterised in that it comprises from 2 to 10,000 mg of a refractory oxide per gram of prepolymer.

55

5. Prepolymer according to any of Claims 1 to 4, characterised in that it is in the form of a powder having a bulk density of 0.3 to 0.55g/cm³.
- 5 6. Process for preparing the prepolymer according to any of Claims 1 to 5, characterised in that the antistatic agent is brought into contact with (a) a catalyst based on at least one transition metal belonging to one of the Groups IV, V or VI of the Periodic Classification of the elements and (b) at least one organometallic compound of a metal of Group II or III of the said Periodic Classification, before and/or during a prepolymerization comprising bringing the said catalyst into contact with at least one C₂-C₁₂ alpha-olefin and with the said organometallic compound, in quantities of from 0.1 to 200g of the
10 antistatic agent per gram atom of the transition metal of the said catalyst and from 0.01 to 100 moles of the said organometallic compound per gram atom of the transition metal of the said catalyst, the prepolymerization being carried out until from 0.1 to 500g of prepolymer are obtained per milligram atom of the transition metal of the said catalyst.
- 15 7. Process according to Claim 6, characterised in that the antistatic agent is brought into contact with (a) the catalyst and (b) the organometallic compound in the presence of a hydrocarbon liquid which is either an inert saturated hydrocarbon or an alpha-olefin.
- 20 8. Process for preparing the prepolymer according to any of Claims 1 to 5, characterised in that the antistatic agent is brought into contact with a prepolymer obtained after a prepolymerization comprising bringing into contact a catalyst based on at least one transition metal belonging to one of the Groups IV, V or VI of the Periodic Classification of the elements with at least one organometallic compound of a metal of Group II or III of the said Periodic Classification and with at least one C₂-C₁₂ alpha-olefin, the prepolymer comprising from 0.002 to 10 milligram atoms of the transition metal of the said catalyst and
25 having an atomic ratio of the metal of the said organometallic compound to the transition metal of the said catalyst from 0.01 to 100, the antistatic agent being contacted with the prepolymer in an amount from 0.1 to 200g per gram atom of the transition metal contained in the prepolymer.
- 30 9. Process according to Claim 8, characterised in that the antistatic agent is brought into contact with the prepolymer in the presence of a hydrocarbon liquid which is either an inert saturated hydrocarbon or an alpha-olefin.
- 35 10. Process for preparing the prepolymer according to any of Claims 1 to 5, characterised in that the antistatic agent (i) is first of all brought into contact with (a) a catalyst based on at least one transition metal belonging to one of the Groups IV, V or VI of the Periodic Classification of the elements and (b) at least one organometallic compound of a metal of Group II or III of the said Periodic Classification before or during a prepolymerization comprising bringing the said catalyst into contact with at least one C₂-C₁₂ alpha-olefin and with the said organometallic compound, in quantities of from 0.05 to 100g of the antistatic agent per gram atom of the transition metal of the said catalyst and from 0.01 to 100
40 moles of the said organometallic compound per gram atom of the transition metal of the said catalyst, the prepolymerization being carried out until from 0.1 to 500g of prepolymer are obtained per milligram atom of the transition metal of the said catalyst, and (ii) is then brought into contact with the prepolymer obtained after the end of the prepolymerization in a quantity ranging from 0.05 to 100g of the antistatic agent per gram atom of the transition metal contained in the prepolymer.
45
- 50 11. Process according to Claim 10, characterised in that the contacting of the antistatic agent with (a) the catalyst and (b) the organometallic compound before or during the prepolymerization and the contacting of the antistatic agent with the prepolymer after the end of the prepolymerization are carried out in the presence of a liquid hydrocarbon which is either an inert saturated hydrocarbon or an alpha-olefin.
- 55 12. Process according to any of Claims 6 to 11, characterized in that the catalyst is either a catalyst of Ziegler-Natta type comprising at least one transition metal selected amongst titanium, vanadium, hafnium, zirconium and chromium and optionally a refractory oxide support, or a catalyst comprising a chromium oxide supported on a refractory oxide and activated by a heat treatment under a non-reductive atmosphere.
13. Process for the gas phase (co-)polymerization of one or more alpha-olefins, characterized in that it is carried out by introducing into the gas phase (co-)polymerization medium the prepolymer according to

any of Claims 1 to 5.

14. Process according to Claim 13, characterised in that the prepolymer is introduced into the gas phase (co-)polymerization medium in the form of a slurry in a hydrocarbon liquid which is either an inert saturated hydrocarbon or an alpha-olefin, or in the form of a dry powder.

Patentansprüche

1. Katalytisch bei einer alpha-Olefin-(Co)-Polymerisation aktives Präpolymer eines oder mehrerer C₂-C₁₂-alpha-Olefine, das aus Teilchen mit einem Massenmitteldurchmesser im Bereich von 50 bis 500 µm besteht und 0,002 bis 10 mg Atome mindestens eines zu einer der Gruppen IV, V oder VI des Periodensystems der Elemente gehörenden Übergangsmetalls pro Gramm Präpolymer, ein antistatisches Mittel und mindestens eine Organometallverbindung eines Metalls der Gruppe II oder III der Periodensystems in einem Atomverhältnis Metall(e) der Organometallverbindung(en)/Übergangsmetall(e) von 0,01 bis 100 umfaßt.
2. Präpolymer nach Anspruch 1, dadurch gekennzeichnet, daß es 0,01 bis 10 mg des antistatischen Mittels pro Gramm Präpolymer umfaßt.
3. Präpolymer nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das antistatische Mittel mindestens eine(s) der Produkte oder Verbindungen, ausgewählt aus:
 - einem Metallsalz einer C₈-C₃₀-Carbonsäure, wobei das Metall aus einem Alkalimetall, einem Erdalkalimetall, Cu, Zn, Cd, Al, Pb, Cr, Mo oder Mn besteht,
 - einem Cr-Salz einer C₁₀-C₂₀-Alkyl- oder Alkenyl-substituierten aromatischen Carbonsäure,
 - einem Cr-Salz einer N-Alkyl- oder N-Alkenyl-anthranilsäure,
 - einem Alkali- oder Erdalkalimetallsalz einer Alkylcarboxylat-substituierten Sulfonsäure,
 - einem alkylierten Phytinsäurepolyethyleniminsalz,
 - einem quaternären Ammoniumsalz von Phytinsäure,
 - einem Copolymer von (i) einer ethylenisch ungesättigten Carbonsäure oder einem ethylenisch ungesättigten Ester mit (ii) einer ethylenisch ungesättigten organischen Base,
 - einem Salz eines Sulfonsäureesters,
 - einem Polyethylenglykolester einer Fettsäure und
 - einem Polyoxyethylenalkylether,
 umfaßt.
4. Präpolymer nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß es 2 bis 10.000 mg eines feuerfesten Oxids pro Gramm Präpolymer umfaßt.
5. Präpolymer nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß es in Form eines Pulvers mit einer Schüttdichte von 0,3 bis 0,55 g/cm³ vorliegt.
6. Verfahren zur Herstellung des Präpolymeren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das antistatische Mittel mit (a) einem Katalysator auf Basis mindestens eines zu einer der Gruppen IV, V oder VI des Periodensystems der Elemente gehörenden Übergangsmetalls und (b) mindestens einer Organometallverbindung eines Metalls der Gruppe II oder III des Periodensystems vor und/oder während einer das Inberührungbringen des Katalysators mit mindestens einem C₂-C₁₂-alpha-Olefin und mit der Organometallverbindung umfassenden Präpolymerisation in Mengen von 0,1 bis 200 g des antistatischen Mittels pro Gramm Atom des Übergangsmetalls des Katalysators und von 0,01 bis 100 Mol der Organometallverbindung pro Gramm Atom des Übergangsmetalls des Katalysators in Berührung gebracht wird, wobei die Präpolymerisation durchgeführt wird, bis 0,1 bis 500 g Präpolymer pro Milligramm Übergangsmetallatom des Katalysators erhalten werden.
7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das antistatische Mittel mit (a) dem Katalysator und (b) der Organometallverbindung in Gegenwart einer Kohlenwasserstoffflüssigkeit, bei der es sich entweder um einen inerten gesättigten Kohlenwasserstoff oder ein alpha-Olefin handelt, in Berührung gebracht wird.

8. Verfahren zur Herstellung des Präpolymeren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das antistatische Mittel mit einem nach einer Präpolymerisation, die ein Inberührungbringen eines Katalysators auf Basis mindestens eines zu einer der Gruppen IV, V oder VI des Periodensystems der Elemente gehörenden Übergangsmetalls mit mindestens einer Organometallverbindung eines Metalls der Gruppe II oder III des Periodensystems und mit mindestens einem C₂-C₁₂-alpha-Olefin umfaßt, erhaltenen Präpolymer, das 0,002 bis 10 mg Atome des Übergangsmetalls des Katalysators umfaßt und ein Atomverhältnis Metall der Organometallverbindung/Übergangsmetall des Katalysators von 0,01 bis 100 aufweist, in Berührung gebracht wird, wobei das antistatische Mittel mit dem Präpolymer in einer Menge von 0,1 bis 200 g pro Gramm Atom des in dem Präpolymer enthaltenen Übergangsmetalls in Berührung gebracht wird.
9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das antistatische Mittel mit dem Präpolymeren in Gegenwart einer Kohlenwasserstofflüssigkeit, bei der es sich entweder um einen inerten gesättigten Kohlenwasserstoff oder ein alpha-Olefin handelt, in Berührung gebracht wird.
10. Verfahren zur Herstellung des Präpolymeren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das antistatische Mittel (i) zuerst mit (a) einem Katalysator auf Basis mindestens eines zu einer der Gruppen IV, V oder VI des Periodensystems der Elemente gehörenden Übergangsmetalls und (b) mindestens einer Organometallverbindung eines Metalls der Gruppe II oder III des Periodensystems vor oder während einer das Inberührungbringen des Katalysators mit mindestens einem C₂-C₁₂-alpha-Olefin und mit der Organometallverbindung umfassenden Präpolymerisation in Mengen von 0,05 bis 100 g des antistatischen Mittels pro Gramm Atom des Übergangsmetalls des Katalysators und von 0,01 bis 100 Mol der Organometallverbindung pro Gramm Atom des Übergangsmetalls des Katalysators, wobei die Präpolymerisation durchgeführt wird, bis 0,1 bis 500 g Präpolymer pro Milligramm Atom des Übergangsmetalls des Katalysators erhalten werden, und (ii) anschließend mit dem nach der Präpolymerisation erhaltenen Präpolymeren in einer Menge im Bereich von 0,05 bis 100 g des antistatischen Mittels pro Gramm Atom des in dem Präpolymeren enthaltenen Übergangsmetalls in Berührung gebracht wird.
11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das Inberührungbringen des antistatischen Mittels mit (a) dem Katalysator und (b) der Übergangsmetallverbindung vor oder während der Präpolymerisation und das Inberührungbringen des antistatischen Mittels mit dem Präpolymeren nach der Präpolymerisation in Gegenwart eines flüssigen Kohlenwasserstoffs, bei dem es sich entweder um einen inerten gesättigten Kohlenwasserstoff oder ein alpha-Olefin handelt, durchgeführt werden.
12. Verfahren nach einem der Ansprüche 6 bis 11, dadurch gekennzeichnet, daß der Katalysator entweder aus einem Katalysator vom Ziegler-Natta-Typ mit mindestens einem aus Titan, Vanadium, Hafnium, Zirkonium und Chrom ausgewählten Übergangsmetall und gegebenenfalls einem Träger aus einem feuerfesten Oxid oder einem Katalysator mit einem auf einem feuerfesten Oxid als Träger befindlichen und durch eine Wärmebehandlung unter einer nicht reduktiven Atmosphäre aktivierten Chromoxid besteht.
13. Verfahren zur Gasphasen-(Co)-Polymerisation eines oder mehrerer alpha-Olefine, dadurch gekennzeichnet, daß es durch Einführen des Präpolymeren nach einem der Ansprüche 1 bis 5 in das Gasphasen-(Co)-Polymerisationsmedium durchgeführt wird.
14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß das Präpolymer in Form einer Aufschlämmung in einer Kohlenwasserstofflüssigkeit, bei der es sich entweder um einen inerten gesättigten Kohlenwasserstoff oder ein alpha-Olefin handelt, oder in Form eines trockenen Pulvers in das Gasphasen-(Co)-Polymerisationsmedium eingeführt wird.

Revendications

1. Prépolymère d'une ou plusieurs alpha-oléfines en C₂ à C₁₂, qui est catalytiquement actif dans une (co-)polymérisation d'alpha-oléfines, le prépolymère se composant de particules ayant un diamètre moyen en masse compris entre 50 et 500 µm et comprenant de 0,002 à 10 millièmes-grammes d'au moins un métal de transition appartenant à l'un des groupes IV, V ou VI de la classification périodique des éléments par gramme de prépolymère, un agent antistatique et au moins un composé organométalli-

que d'un métal des groupes II ou III de ladite classification périodique dans un rapport atomique du métal ou des métaux du ou des composés organométalliques au(x) métal(x) de transition de 0,01 à 100.

- 5 2. Prépolymère selon la revendication 1, caractérisé en ce qu'il comprend de 0,01 à 10 mg de l'agent antistatique par gramme de prépolymère.
3. Prépolymère selon la revendication 1 ou 2, caractérisé en ce que l'agent antistatique comprend au moins un des produits ou composés choisis parmi:
 - 10 - un sel métallique d'un acide carboxylique en C_8 à C_{30} , le métal étant un métal alcalin, un métal alcalino-terreux, Cu, Zn, Cd, Al, Pb, Cr, Mo ou Mn,
 - un sel de Cr d'un acide carboxylique aromatique substitué par un alcényle ou alkyle en C_{10} à C_{20} ,
 - un sel de Cr d'un acide N-alkyl ou N-alcénylanthranilique,
 - 15 - un sel métallique alcalin ou alcalino-terreux d'un acide sulfonique substitué par un alkylcarboxylate,
 - un sel de poly(éthylène imine) et d'acide phytique alkylé,
 - un sel d'ammonium quaternaire de l'acide phytique,
 - un copolymère (i) d'un acide carboxylique éthyléniquement insaturé ou d'un ester éthyléniquement insaturé avec (ii) une base organique éthyléniquement insaturée,
 - 20 - un sel d'un ester d'acide sulfonique,
 - un ester de polyéthylèneglycol et d'un acide carboxylique gras, et
 - un éther alkylque de poly(oxyde d'éthylène).
- 25 4. Prépolymère selon l'une quelconque des revendications 1 à 3, caractérisé en ce qu'il comprend de 2 à 10 000 mg d'un oxyde réfractaire par gramme de prépolymère.
5. Prépolymère selon l'une quelconque des revendications 1 à 4, caractérisé en ce qu'il est sous forme d'une poudre ayant une masse volumique apparente de 0,3 à 0,55 g/cm³.
- 30 6. Procédé pour préparer le prépolymère selon l'une quelconque des revendications 1 à 5, caractérisé en ce que l'agent antistatique est mis en contact avec (a) un catalyseur à base d'au moins un métal de transition appartenant à l'un des groupes IV, V ou VI de la classification périodique des éléments, et (b) au moins un composé organométallique d'un métal des groupes II ou III de ladite classification périodique, avant et/ou pendant une prépolymérisation comprenant la mise en contact dudit catalyseur avec au moins une alpha-oléfine en C_2 à C_{12} et avec ledit composé organométallique, à raison de 0,1 à 200 g de l'agent antistatique par atome-gramme du métal de transition dudit catalyseur et de 0,01 à 100 moles dudit composé organométallique par atome-gramme du métal de transition dudit catalyseur, la prépolymérisation étant effectuée jusqu'à ce que l'on obtienne 0,1 à 500 g de prépolymère par milliatome-gramme du métal de transition dudit catalyseur.
- 35 7. Procédé selon la revendication 6, caractérisé en ce que l'agent antistatique est mis en contact avec (a) le catalyseur et (b) le composé organométallique en présence d'un liquide hydrocarboné qui est soit un hydrocarbure saturé inerte, soit une alpha-oléfine.
- 45 8. Procédé pour préparer le prépolymère selon l'une quelconque des revendications 1 à 5, caractérisé en ce que l'agent antistatique est mis en contact avec un prépolymère obtenu après une prépolymérisation comprenant la mise en contact d'un catalyseur à base d'au moins un métal de transition appartenant à l'un des groupes IV, V ou VI de la classification périodique des éléments avec au moins un composé organométallique d'un métal des groupes II ou III de ladite classification périodique et avec au moins une alpha-oléfine en C_2 à C_{12} , le prépolymère comprenant de 0,002 à 10 milliatomes-grammes du métal de transition dudit catalyseur et ayant un rapport atomique du métal dudit composé organométallique au métal de transition dudit catalyseur de 0,01 à 100, l'agent antistatique étant mis en contact avec le prépolymère à raison de 0,1 à 200 g par atome-gramme du métal de transition contenu dans le prépolymère.
- 50 9. Procédé selon la revendication 8, caractérisé en ce que l'agent antistatique est mis en contact avec le prépolymère en présence d'un liquide hydrocarboné qui est soit un hydrocarbure saturé inerte, soit une
- 55

alpha-oléfine.

10. Procédé pour préparer le prépolymère selon l'une quelconque des revendications 1 à 5, caractérisé en ce que l'agent antistatique (i) est tout d'abord mis en contact avec (a) un catalyseur à base d'au moins un métal de transition appartenant à l'un des groupes IV, V ou VI de la classification périodique des éléments et (b) au moins un composé organométallique d'un métal des groupes II ou III de ladite classification périodique avant ou pendant une prépolymérisation comprenant la mise en contact dudit catalyseur avec au moins une alpha-oléfine en C₂ à C₁₂ et avec ledit composé organométallique, à raison de 0,05 à 100 g de l'agent antistatique par atome-gramme du métal de transition dudit catalyseur et de 0,01 à 100 moles dudit composé organométallique par atome-gramme du métal de transition dudit catalyseur, la prépolymérisation étant effectuée jusqu'à ce que l'on obtienne 0,1 à 500 g de prépolymère par milliatome-gramme du métal de transition dudit catalyseur, et (ii) est ensuite mis en contact avec le prépolymère obtenu après la fin de la prépolymérisation en une quantité comprise entre 0,05 et 100 g de l'agent antistatique par atome-gramme du métal de transition contenu dans le prépolymère.
11. Procédé selon la revendication 10, caractérisé en ce que la mise en contact de l'agent antistatique avec (a) le catalyseur et (b) le composé organométallique avant ou pendant la prépolymérisation et la mise en contact de l'agent antistatique avec le prépolymère après la fin de la prépolymérisation sont effectuées en présence d'un hydrocarbure liquide qui est soit un hydrocarbure saturé inerte, soit une alpha-oléfine.
12. Procédé selon l'une quelconque des revendications 6 à 11, caractérisé en ce que le catalyseur est soit un catalyseur de type Ziegler-Natta comprenant au moins un métal de transition choisi parmi le titane, le vanadium, l'hafnium, le zirconium et le chrome et éventuellement, un support d'oxyde réfractaire, ou un catalyseur comprenant un oxyde de chrome porté sur un oxyde réfractaire et activé par un traitement thermique sous une atmosphère non réductrice.
13. Procédé pour la (co-)polymérisation en phase gazeuse d'une ou plusieurs alpha-oléfines, caractérisé en ce qu'il est effectué en introduisant dans le milieu de (co-)polymérisation en phase gazeuse le prépolymère selon l'une quelconque des revendications 1 à 5.
14. Procédé selon la revendication 13, caractérisé en ce que le prépolymère est introduit dans le milieu de (co-)polymérisation en phase gazeuse sous forme d'une suspension dans un liquide hydrocarboné qui est soit un hydrocarbure saturé inerte ou une alpha-oléfine, soit sous forme d'une poudre sèche.